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TECHNICAL NOTES

MEASUREMENT OF THERMAL CONDUCTIVITY OF MOLTEN SALTS IN THE RANGE 100–500°C

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NOMENCLATURE

c_p	heat capacity at constant pressure
d	differentiation operator
e	thickness of a layer
h	heat transfer coefficient
q	heat flow
R	electrical resistance
t	time
T	Kelvin temperature
v	velocity of fluid
∇	gradient operator.

Greek symbols

Δ	vertical difference
δ	increment
κ	thermal diffusivity
λ	thermal conductivity
ρ	density.

Subscripts

c	critical
F	fluxmeter
o	oil.

1. INTRODUCTION

On account of the growth of new forms of energy and of the problems of energy saving which have arisen during recent years, heat storage has become very important. So the knowledge of the physical properties of liquids used, and particularly the thermal conductivity, is very important. Among the liquids, which can be considered for use, the molten salts seem to be very interesting on account of their large latent heat of melting, their stability over a relatively wide range of temperatures, their good heat capacity, and their large diversity of melting temperatures from one salt to another.

Besides the inherent difficulties in the liquid state, measurements of thermal conductivity of molten salts are still more difficult because these liquids are corrosive and their melting temperatures are generally high. Furthermore, they are good electrical conductors and that prohibits the use of methods which are very convenient for other liquids such as the hot-wire method. In the latter method an electric current of constant intensity passes through a platinum wire. It is shown that [1–3], if the time is shorter than a critical value t_c, the increase δR of the electrical resistance is a linear function of $\ln(\delta t)$ and that the slope of the function δR vs $\ln(\delta t)$ is proportional to λ^{-1}. The wire is vertical and as soon as the current is established there is a horizontal temperature gradient. So the fluid stability is impossible: the convection occurs at once. The fluid rises up the wire and goes down the walls of the vessel. But if $t < t_c$ the horizontal component of ∇T is small and $\mathbf{v}\cdot\nabla T$ can be neglected. Beyond t_c the quantity $\mathbf{v}\cdot\nabla\mathbf{T}$ is no longer negligible in the energy equation and the determination of λ becomes impossible. Strictly speaking, t_c is zero, but in practice it can be supposed that $\mathbf{v}\cdot\nabla\mathbf{T} = 0$ as long as δR is a linear function of $\ln(\delta t)$. In this method precise knowledge of the electrical power in the wire is needed: only electrical insulating liquids can be studied because, in this case, there is no derivation through the liquid. Besides, δR is measured from the potential difference at the ends of the wire. It is obvious that if the liquid is polarizable the difference of potential is simultaneously due to the heating of the wire, to the polarization of the surrounding liquid and to the derivation in the fluid: it is impossible to separate the three mechanisms. We measured the apparent thermal conductivity of a solution $H_2O + NaCl$ as a function of NaCl concentration. As expected the results did not agree with the data of λ found in the literature. This method is not suitable for measurements in ionic liquids and especially in molten salts as it has been shown in particular by White and Davis [4].

The other methods require either the fluid to be motionless or the velocity to be strictly perpendicular to the temperature gradient ($\mathbf{v}\cdot\nabla\mathbf{T} = 0$).

For instance the method proposed by Angstroem [5] allows the measurement of thermal diffusivity from the determination of phase and the attenuation of a harmonic thermic perturbation. It is a variable regime method, and little used because a perfectly motionless fluid is needed (as in many techniques) and because it only provides κ. To reach λ it is also necessary to measure ρ and c_p, but these measurements are as awkward to obtain as those of λ.

The same remarks are also valid for all the experiments providing the thermal diffusivity, and in particular the wave-front shearing interferometry. It is otherwise a very interesting technique because only a very small rise in temperature is needed for the heat source (about 0.2°C) and the optical method of determination is sensitive. It was applied to molten salts by Gustafsson *et al.* [6] and Okada and co-workers [7, 8].

In the independent time method a constant thermal flow passes through a liquid layer. Two techniques can be considered: an 'absolute' technique in which the heat flow and the thermal gradient are directly measured, or a relative technique in which only two temperature gradients are measured. The first of these gradients is applied to a thermal conductivity standard and the other to the liquid to be studied.

Whatever the selected technique may be the convective movements in the liquid must be eliminated. For that purpose it is absolutely necessary to avoid horizontal thermal gradients because they induce density variations which destabilize the fluid. Likewise a vertical descending gradient is also destabilizing because it induces inversions of density and beyond a certain temperature threshold convection occurs. The only non-destabilizing heating in a fluid layer occurs when the liquid is very uniformly heated from above. From the preceding considerations we built a conductimeter on the following principle.

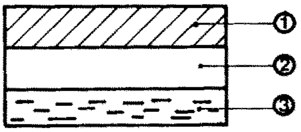

Fig. 1. Principle of the conductimeter: (1) fluxmeter; (2) thermal bond; (3) liquid to be studied.

2. PRINCIPLE

A vertical, constant heat flow goes down through two layers (Fig. 1). The first one is a solid and is the standard of conductivity called the fluxmeter. The second one is the liquid to be studied. The thermal bond between these two layers is effected by a very good conducting solid.

Because the thermal transfer is only conductive and if the thermal contacts are perfect, the balance of heat flow through the layers is

$$\lambda_F \frac{\Delta T_F}{e_F} = \lambda \frac{\Delta T}{e} + h(\delta T + \delta T_F). \qquad (1)$$

In practice the apparatus is regulated so that the horizontal temperature differences δT and δT_F are nil and the heat conductivity λ is easily found from the measurement of ΔT, ΔT_F, e, e_F and from the known value λ_F of the fluxmeter.

3. APPARATUS

A schematic diagram of the apparatus is shown in Fig. 2. Two independent cylinders are the essential parts of the conductimeter. The cell containing the molten salt is between the two cylinders in the central part.

The upper part is constituted, from the top to the centre by:

(1) A water tank (A) made of stainless steel.

(2) A disc (F) made of stumatite.*

(3) A disc (B) made of copper which ensures the thermal bond between (F) and the fluxmeter (G) also made of stumatite. A heating spiral resistance placed on the upper surface of (B) produces the descending vertical heat flow. The electric power given by this resistance is constant thanks to a regulating apparatus designed and built in our laboratory.

(4) A disc (C) also made of copper which ensures the thermal bond between (G) and the liquid to be studied.

The whole is kept in position by the cylinder (E) made of stumatite which is fixed to (C). Several helicoidal resistances are set on the lateral surface. They are independently regulated so that the horizontal temperature gradients between (G), (C) and (E) are nil. Finally a jacket (D) envelops the whole upper part. Four resistances are set on its lateral surface, they are separately regulated.

The lower part is composed of:

(1) The cell (J) made of copper. As for (C) all the parts in contact with the molten salt are covered with a chromium film to prevent corrosion. A guard ring around the cell prevents the deformation of isotherms in the liquid close to the rim. A second ring around the guard ring acts as a reservoir: it maintains a constant volume of salt in the cell.

(2) A piling-up of pieces (N), (K), (O) and (L) which have the same role as (G), (B), (F) and (A), respectively. The role of (L) is to create a cold surface on (O) which is symmetrical to the warm surface on (F). The temperature gradient through the liquid is fixed from the respective temperatures on (F) and (L).

The whole is kept in position by (P) and (M) which are made of stumatite.

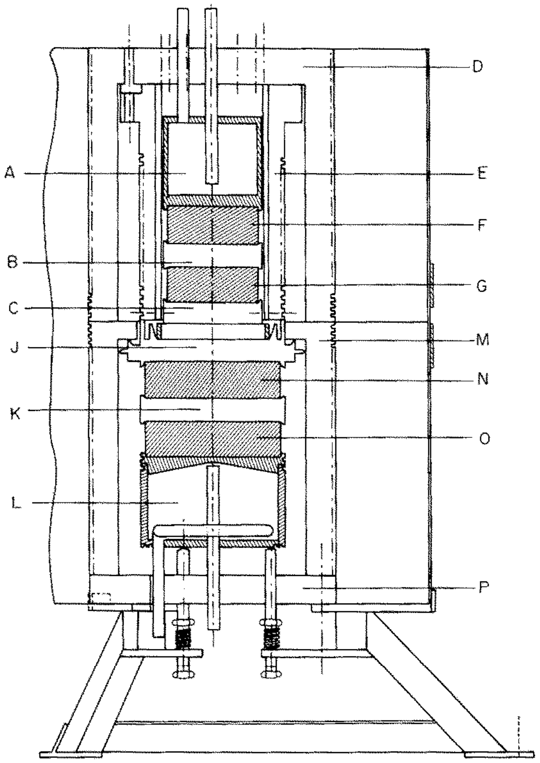

Fig. 2. Schema of the conductimeter: (A), (L), watertanks; (B), (C), (K), discs made of copper and covered with a film of chromium; (F), (N), (O), discs made of stumatite; (D), (M), (P), (E), jackets made of stumatite; (G), fluxmeter; (J), cell containing the liquid to be studied.

The checking and the measurement of temperature gradients are performed by 28 thermocouples, which are put on the surfaces of (G), (C), (J), (E) and (D). Some of them are set in opposition to check the gradients accurately. Measurements are automatically carried out using a controlled data acquisition system. For further calculations the only data used were those obtained after a minimum of 3 h in a state of equilibrium.

The use of a relative technique requires the calibration of the apparatus. It must be noted that, in practice, λ_F is the apparent thermal conductivity which includes the thermal resistances between the different parts of (G), (C), the liquid and (T). The standard of conductivity used for calibration was a silicone oil with a thermal conductivity $\lambda_0 = 0.147\ \mathrm{W\ m^{-1}\ K^{-1}}$ [9]. We

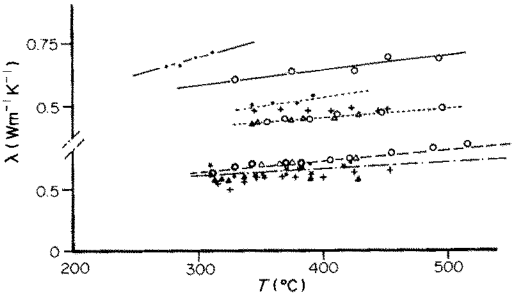

Fig. 3. Thermal conductivity of pure molten salts: ——, $NaNO_2$; ------, KNO_3; -·-— —— and —·—·—·—, $NaNO_3$; ○, present work; ●, Bloom *et al.* [12]; +, Gustafsson *et al.* [6]; △, White and Davis [4]; ▲, McLaughlin [14]; ★, Odawara *et al.* [7]; —·—·—·-, McDonald [13].

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* It is a natural ceramic which has many possible uses because it has many qualities: easy machining, good resistance to heat and to chemical products, insulating material, etc.

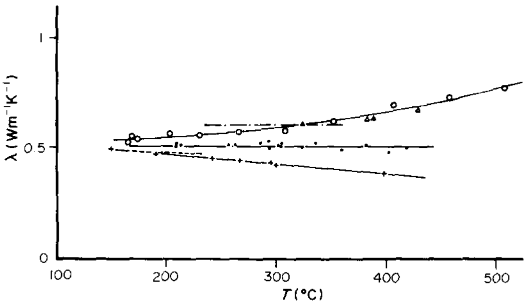

FIG. 4. Thermal conductivity of Hitec: ○, present work; △, Hoffman [18]; ●, Odawara *et al.* [7]; +, Turnbull [15]; —·—·—, Powers [17]; ------, Berthet and Peninou [16].

verified this value, using the hot-wire method. The apparent value of λ_F was 1.3 ± 0.07 W m^{-1} K^{-1} in the range 150–350°C. Taking into account thermic resistances, the concordance with λ of stumatite (1.4 W m^{-1} K^{-1}) can be considered as fair.

4. RESULTS AND DISCUSSION

The thermal conductivity of pure salts $NaNO_3$, KNO_3, $NaNO_2$ and of their mixture called Hitec was measured. The latter is the ternary eutectic (0.53 KNO_3, 0.07 $NaNO_3$, 0.40 $NaNO_2$, wt.%). It was studied because it is very important in the energy storage and heat transfer techniques [10]. Expressions of λ as a function of temperature are shown in Table 1. In contradiction with the rough model of Bridgman [11] λ is an increasing function of T. The concordance with previous results found in the literature is variable, depending on the technique used. For the pure salts (Fig. 3) the difference with the results of Bloom *et al.* [12] can be up to 15%. But they used the coaxial cylinders method and it seems, as White and Davis [4] mentioned, that they did not take all the precautions necessary to avoid convection. White and Davis used the same technique but they took care to prevent convection. Their results coincide with ours and are slightly greater than those of McDonald [13] who used the same method, and greater than those of McLaughlin [14] obtained using a hot-wire method which is not suitable for molten salts.

Other interesting results have been obtained by Odawara *et al.* [7] and Gustafsson *et al.* [6] using an optical interferometric method. They calculated the heat conductivity from their thermal diffusivity data and Odawara *et al.* found it to be almost independent of temperature. In the studied temperature range the difference with our results is more than 4%. Gustafsson *et al.*'s results are similar to our data especially for KNO_3.

As far as Hitec is concerned (Fig. 4) a greater dispersion between the results of different authors is observed. At 150°C almost all the data found in the literature have approximately the same value (0.5 W m^{-1} K^{-1} $< \lambda <$ 0.6 W m^{-1} K^{-1}), but the temperature coefficients are very different. For instance Turnbull [15] found a decrease in λ with T ($d\lambda/dT = -5 \times 10^{-4}$ W m^{-1} K^{-2}) as did Berthet and Peninou [16] but using the hot-wire method. According to Odawara *et al.* [7], λ is practically independent of T ($d\lambda/dT = -4.7 \times 10^{-5}$ W m^{-1} K^{-2}) as with Powers [17]. On the other hand Hoffman [18] found an increase in λ with T very close to our results.

Table 1. Temperature dependence of thermal conductivity expressed through a polynomial equation

$\lambda = a + bT + cT^2$ (T[K], λ[W m^{-1} K^{-1}])

Salt	*a*	*b*	*c*
KNO_3	0.18	4.04×10^{-4}	0
$NaNO_3$	0.28	5.0×10^{-4}	0
$NaNO_2$	0.25	5.80×10^{-4}	0
Hitec	0.78	-1.25×10^{-3}	1.6×10^{-6}

According to Bloom *et al.* [12] and McDonald [13] the temperature dependence of the thermal conductivity of a molten mixture of $NaNO_3$–KNO_3 is much the same as that of the pure salts. Iwadate *et al.* [8] came to the same conclusion for the mixture KNO_3–$NaNO_2$. Therefore, it is reasonable to suppose that the thermal conductivity of Hitec is also an increasing function of temperature, in concordance with the present experimental results.

5. COMMENT

All the preceding experiments were carried out when the molten salt was uniformly heated from above, so no convection occurred. On the contrary if the liquid is uniformly heated from below, the convection occurs beyond a critical value of the temperature difference. We studied the thermal transfer in this last case. The ionic liquid used was Hitec at 165°C.

We measured the heat flow through the fluid as a function of the temperature difference between the two limiting surfaces. A linear regression method provides the equation $q = f(\Delta T)$ of a straight line which meets the straight line corresponding to the only heat conduction at a point such as $\Delta T = 0.70$°C. This value corresponds to the critical Rayleigh number 1870 when the theoretical value is 1707. Taking into account the experimental errors this result can be considered as fair and as indirect proof of the correctness of the thermal conductivity measurement.

6. CONCLUSION

This apparatus prohibits the convective phenomena and provides the thermal conductivity in a wide temperature range (from 100 to 500°C). It was built for ionic liquids but all kinds of liquids can be studied. It takes a long time to reach equilibrium but it is convenient to use.

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A STUDY OF THE VARIATION OF THE PRESSURE IN A NATURAL CIRCULATION LOOP

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NOMENCLATURE

c	specific heat
D	dimensionless parameter, $2\pi Rh/crV\rho_w$
f	friction coefficient, $2\tau_w/\rho_w v^2$
g	acceleration of gravity
h	heat transfer coefficient per unit of length
p	dimensionless pressure
Δp	pressure difference, $p(\theta,\tau)-p(0,\tau)$
p_t	dimensionless total pressure, $2p_t^*/\rho_w V^2$
p_t^*	total pressure
q	heat flux, cf. Fig. 1
R	radius of the circular loop, cf. Fig. 1
Re	Reynolds number, $\rho_w v 2r/\mu$
r	radius of the toroid, cf. Fig. 1
T	temperature
T_w	constant wall temperature for the upper loop, cf. Fig. 1
t	time
V	characteristic velocity, $(g\beta Rrq/2\pi c\mu)^{1/2}$
v	velocity of the fluid
w	dimensionless velocity, v/V.

Greek symbols

β	thermal expansion coefficient
Γ	dimensionless parameter, $16\pi\mu R/\rho_w r^2 V$
θ	space coordinate, cf. Fig. 1
μ	absolute viscosity
ρ_w	reference density evaluated at the wall temperature, T_w
ϕ	dimensionless temperature, $h(T-T_w)/q$
τ	dimensionless time, $Vt/2\pi R$
τ_w	shear stress, $f\rho_w v^2/2$.

Subscripts

avg	average over the loop
d	dynamic
s	static
ss	steady state.

INTRODUCTION

A study has been made of the steady-state and transient pressure variation in a closed toroidal natural convection loop (cf. Fig. 1). The loop is heated over the lower half and cooled over the upper half. The resulting density variation causes the fluid to flow. Previous studies of toroidal loops have presented the temperature distributions, flow rates and stability characteristics [1–9]. A number of related studies have also been carried out [10–16]. The present work differs from previous studies in that the pressure distribution is now presented. Limiting analytical expressions have also been derived for the steady-state pressure distributions. To aid in the understanding of the results, the temperature distributions have also been presented along with the limiting expressions [3].

ANALYSIS

The toroidal loop is heated with a constant flux, q, over the lower half, $\pi < \theta < 2\pi$, and cooled by maintaining a constant wall temperature, T_w, over the upper half, $0 < \theta < \pi$. The flow is assumed to be laminar and in the counter-clockwise direction. The dimensionless forms of the momentum and energy equations are [1–3]:

$$\frac{\partial p_t}{\partial \theta} = -\frac{1}{\pi}\frac{\mathrm{d}w}{\mathrm{d}\tau} - \frac{2gR}{V^2}\cos\theta + \frac{\pi}{2}\frac{\Gamma}{D}\phi\cos\theta - \frac{\Gamma}{\pi}w, \quad (1)$$

and

$$\frac{\partial \phi}{\partial \tau} + 2\pi w\frac{\partial \phi}{\partial \theta} = \begin{cases} -2D\phi, & 0 < \theta < \pi, \quad (2a) \\ 2D, & \pi < \theta < 2\pi. \quad (2b) \end{cases}$$

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